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(54) UV-CURABLE PAINT COMPOSITION AND PROCESS FOR ITS APPLICATION TO GLASS SUBSTRATES

(57) An ultraviolet radiation curable organic ink composition, comprising 80% to 95% by weight of an epoxy-polyurethane-based ink; 0.5% to 8% by weight of an additive including a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes; 1% to 7% by weight

of a water resistant agent made from low and intermediate molecular weight polyamide which is recommended to be added just before applying the prepared ink composition because this composition, once prepared, lasts less than 8 hours; and an adhesion promoter primer including 0.15% to 3% by weight of a silane

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Description

BACKGROUND OF THE INVENTION.

A. FIELD OF THE INVENTION.

[0001] The present invention relates to an organic ink composition for a glass substrates and a process for its application and, more specifically to an organic ink composition of the type which is curable by ultra-violet radiation, for printing labels, designs or any other decoration on glass bottles,

B. DESCRIPTION OF THE RELATED ART.

[0002] There are some known inorganic and organic pigment compositions in the market, which provide an acceptable coloration mainly for the decoration of plastic and paper articles. However, those pigment compositions have not been properly applied in glass substrates mainly because its weak resistance to water, solvents, abrasion, etc.

[0003] There is a number of well known radiation curable ink compositions for screen printing, including metallic pigments such as copper, silver, cadmium, chromium manganese, etc. Examples of such ink compositions are disclosed in U. S. patents No. 3,957,694 ; 3,968,056 and 3,989,644 all of Bolon et al, mainly suitable for screen printing on printed circuits.

[0004] It has been an increased interest of glass makers, specifically of glass bottle makers, to use organic inks for labeling or decorating glass bottles, mainly for environmental preservation purposes and reduce the energy needs, as well as for complying with ambient regulations.

[0005] It is also known a number of organic compositions, pigmented or not which are applied and cured by ultra-violet to infra-red radiation, for the most diverse purposes such as providing privacy, solar radiation control, abrasion strengthening, etc., examples of these organic compositions are disclosed in the U. S. patents No. 4,923, 754 and 4,946,874 both of Lee et al; 5,514,521 of Kobayashi; 5,178,952 of Yamamoto et al, and 5,262,450 of Vera et al.

[0006] These pigments or coatings are commonly limited to plastic and paper substrates, printed circuits, etc., but they could not been used for glass applications because of a lack of adhesion or anchoring to the very smooth surface of the glass substrates, as well as because of their poor resistance to the water, solvents and abrasion for rough handling

[0007] U. S. patent No. 5,731,359 of Kamen et al, disclose a pigmented ink composition including a radiation curable component and a pyrrolopyrrol or isoindoline pigment, to provide a red or yellow color, which apparently can be applied by hot stamping from a foil or directly to a substrate and cured by radiation.

[0008] Those inks apparently has been suitable for application on disposable (no-returnable) glass bottles.

[0009] Therefore, some adhesion promoters, photoinitiator such as the Irgacure 184 from Ciba Geigy, strengthening agents, storage stabilizers, photosensitizers, crosslinking agents and so forth, have been introduced into the ink compositions and coatings in order to improve their resistance to the filling process, the multiple alkaline washing process and rough handling, but sill they have not been considered suitable for imparting the desired properties for application to returnable glass bottles.

[0010] In accordance with the present invention, it is provided an ultraviolet radiation curable organic ink composition, comprising 80% to 95% by weight of an epoxy-polyurethane-based ink; 0.5% to 8% by weight of an additive including a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes; 1% to 7% by weight of an additive which improves the water resistance, made from low and intermediate molecular weight polyamide which is recommended to be added just before applying the prepared ink composition because this composition, once prepared, lasts 8 hours at most; and an adhesion promoter which can be added to the ink formula or used as a primer to be applied to the glass substrate before the decoration, and which includes a silane in a concentration of 0.15% to 3% by weight; which, among others:

is specifically suitable for glass substrates;

has a desired strengthening to the washing, before and after the filling process, as well as a suitable resistance to the abrasion and heavy duty to which non-returnable glass bottles are subjected;

can be calcined at the furnace when it is recycled as cullet into a molten glass mass, without affecting the properties of the glass mass because it does not contain toxic metals such as lead, cadmium, hexavalent chromium, etc.;

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is environmentally suitable because it does not generate noxious combustion gases nor hot-house gases;

reduces the ink consumption because it has a specific gravity which is about four times less heavier than the vitrifiable ceramic paints which have commonly been used for the decoration of glass bottles;

provides a greater yield per weight unit and saves energy and space because it does not need big furnaces for heating the paint;

provides more intense and bright colors and a more wide range of colors than the ceramic paints;

has a better adherence to the glass substrate because of the presence of the adhesion promoter in the ink or in the primer applied to the surface of the glass bottles and because of the specific application method by which it is applicable.

[0011] Furthermore, in accordance with the present invention, it is provided a process for the preparation and application of the above disclosed ultraviolet radiation curable organic ink composition, comprising: a) preparing an ultra-violet radiation curable ink composition by mixing 80% to 95% by weight of an epoxy-polyurethane-base ink composition; and 0.5% to 8% by weight of an additive prepared from a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes, strongly stirring the mixture; b) adding from 1 to 7% by weight of an additive that improves the water resistance, made from low and intermediate molecular weight polyamide, just before applying the prepared ink composition because this composition, once prepared, lasts a maximum of 8 hours; c) adding an adhesion promoter primer composition comprising 0.15% to 3% by weight of a silane; e) applying the prepared ink composition on the glass substrate, by serigraphy, tampography or the like and curing the ink composition by exposing the coated surface to an ultraviolet radiation; f) heating the substrate by passing it through a heatinglehr to increase the temperature of the substrate between 100° to 160°C; and g) applying a lubricant agent including an oleic acid-based product as a gas or vapor, and/or spraying an aqueous emulsion of an ethoxylated polyethylen-derivative.

[0012] So that the above composition in combination with the disclosed process for its preparation and application, provides all the above disclosed advantages over the known prior art.

SUMMARY OF THE INVENTION

[0013] It is therefore a main object of the present invention, to provide an ultraviolet radiation curable organic ink composition specially suitable for glass substrates, which has a desired strengthening to the washing with water, before and after the filling process, as well as a suitable resistance to the severe abrasion and heavy duty to which non-returnable glass bottles are subjected;

[0014] It is also a main object of the present invention, to provide an ultraviolet radiation curable organic ink composition, of the above disclosed nature, which may be calcined at a furnace when it is recycled as cullet into a molten glass mass, without affecting the properties of the glass mass because it does not contain toxic metals such as lead, cadmium, hexavalent chromium, etc. and which makes it is environmentally suitable because it does not generate noxious combustion gases nor hot-house gases;

[0015] It is also a main object of the present invention, to provide an ultraviolet radiation curable organic ink composition, of the above disclosed nature, which reduces the ink consumption because it has a specific gravity which is about four times less heavier than the vitrifiable ceramic paints which have commonly been used for the decoration of glass bottles, providing a greater yield per weight unit and saves energy and space because it does not need big furnaces for heating the paint;

[0016] It is still a main object of the present invention, to provide an ultraviolet radiation curable organic ink composition, of the above disclosed nature, which provides more intense and bright colors and a more wide range of colors than the ceramic paints.

[0017] It is additionally a main objective of the present invention, to provide a process for the preparation and application of an ultraviolet radiation curable organic ink composition specially suitable for glass substrates, by which all of the above desired disclosed properties are imparted to the glass substrates, products or bottles.

[0018] These and other additional objects and advantages of the present invention will be evident to those persons having ordinary skill in the art, from the following detailed description of the invention with reference to specific embodiments thereof.

DETAILED DESCRIPTION OF THE INVENTION.

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[0019] In accordance with the present invention, it is provided an ultraviolet radiation curable ink composition comprising:

5 an ultra-violet radiation curable ink composition including 80 to 95% by weight of an epoxy-polyurethane-based ink; and 0.5% to 8% by weight of an additive including a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes;

1 to 7% by weight of an additive that improves the water resistance, made from low and intermediate molecular weight polyamide, to be added just before applying the prepared ink composition because this composition, once prepared, lasts less than 8 hours; and

an adhesion promoter primer including 0.15% to 3% by weight of a silane.

15 **[0020]** As to the process for the preparation and application of the above disclosed ultraviolet radiation curable organic ink composition, in a preferred embodiment thereof, this comprises:

20 a) preparing an ultra-violet radiation curable ink composition including mixing 80% to 95% by weight of an epoxy-polyurethane-base ink; and 0.5% to 8% by weight of an additive prepared from a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes, strongly stirring the mixture;

b) adding from 1 to 7% by weight of a water resistant agent made from low and intermediate molecular weight polyamide, just before applying the prepared ink composition because this composition, once prepared, lasts a maximum of 8 hours;

25 c) adding an adhesion promoter primer composition comprising 0.15% to 3% by weight of a silane;

d) applying the prepared ink composition on the glass substrate, by serigraphy, tampography or the like;

30 e) curing the ink composition by exposing the coated surface to an ultraviolet radiation;

f) heating the substrate by passing it through a heatinglehr to increase the temperature of the substrate between 100° to 160°C; and

35 g) applying a lubricant agent including an oleic acid-based product as a gas or vapor, and spraying an aqueous emulsion of an ethoxiated polyethylen-derivative, on the portion of the glass substrate including the ink composition.

40 **[0021]** In another embodiment of the invention, it is convenient to prepare separately the adhesion promoter primer composition by adding 70% to 97% by weight of demineralized water and %0 to 19.4% by weight of ethyl alcohol and 0.15 to 3% of silane under stirring, and apply it as a thin layer on the glass substrate, before applying the ultraviolet curable organic ink composition, in order to improve the adhesion thereof, and drying said adhesion promoter primer composition on the glass substrate.

45 **[0022]** Said epoxy-polyurethane-base ink, can be selected from different colors, when red color is desired, this is selected from the family of monoazo pigments such as those known as cd-photoflex from the company Sericol, Inc., specifically that sold under the trademark Graftol 210; Red 2000 CD-JC-2455; Red Rubine CD-155; Intensive Red CD-141; Heat Red CD-180, all from the company Sericol, Inc.

[0023] The white color is selected from the family of the titanium dioxide, specifically those sold under the specifications Opaque White CD-311 also by Sericol Inc.

50 **[0024]** Other colors are Yellow Medium CD-123; Yellow Lemon CD-111; Silver Gray CD-302; Black Shadow CD-SB; Opaque Black CD-301; Reflex Blue CD-205; Blue Process CD-190; and others.

[0025] The additive including the mixture of polyethylenic waxes and polytetrafluoroethylenic waxes known as "PTFE" are selected from those sold as Polifluo XF-523 from the company Micropowders, Corp, the Series TL from Harwick Standard Chemical, Polipenco from Polymer Corporation and Whitcon from Whitford Chemical Corp., and others.

55 **[0026]** The water resistant agent made from low and intermediate molecular weight polyamide is selected from that sold as Kaeropox, and "Water Resistance Agent" from Sericol, Inc.,

[0027] The adhesion promoter primer is selected from those sold as Z-6011, Z-6032, both from Dow Corning, A-

1100 from Witco, or similar, or a mixture thereof.

[0028] And finally, the lubricant agent including an oleic acid-based product is selected from that sold as AP-5 from US-CAN.

[0029] Thus, it is to be understood that, because of the properties of the ultraviolet curable organic ink composition, it is convenient to prepare and apply the composition a few hours before it is applied.

[0030] Furthermore, it is to be understood that the invention is not limited to the above disclosed specific embodiments of the composition and of the process for preparing and applying it to the glass substrates, and that the persons having ordinary skill in the art will be able to introduce changes into the components and steps in view of the teachings of this invention, which will be within the true scope of the invention as claimed in the following.

Claims

1. An ultraviolet curable organic ink composition for glass substrates, comprising:

an ultra-violet radiation curable ink composition including 80 to 95% by weight of an epoxy-polyurethane-based ink; and 0.5% to 8% by weight of an additive including a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes;

1 to 7% by weight of a water resistant agent made from low and intermediate molecular weight polyamide, to be added just before applying the prepared ink composition because this composition, once prepared, lasts less than 8 hours; and

an adhesion promoter primer including 0.15% to 3% by weight of a silane.

2. The ultraviolet curable organic ink composition in accordance with claim 1, wherein when the adhesion promoter primer composition is to be applied to the glass substrate before the ink composition, and includes 0.15% to 3% by weight of a silane; 70% to 97% by weight of demineralized water and 0% to 19.4 % by weight of ethyl alcohol.

3. A process for applying an ultraviolet curable ink composition to a substrate, comprising:

a) preparing an ultra-violet radiation curable ink composition by mixing 80% to 95% by weight of an epoxy-polyurethane-base ink; and 0.5% to 8% by weight of an additive prepared from a mixture of polyethylenic waxes and polytetrafluoroethylenic waxes, strongly stirring the mixture;

b) adding from 1 to 7% by weight of a water resistant agent made from low and intermediate molecular weight polyamide, just before applying the prepared ink composition because this composition, once prepared, lasts less than 8 hours;

c) adding an adhesion promoter primer composition comprising 0.15% to 3% by weight of a silane;

d) applying the prepared ink composition on the glass substrate, by serigraphy, tampography or the like;

e) curing the ink composition by exposing the coated surface to an ultraviolet radiation;

f) heating the substrate by passing it through a heating lehr to increase the substrate temperature between 100° to 160°C; and

g) applying a lubricant agent including an oleic acid-based product as a gas or vapor, and/or spraying an aqueous emulsion of an ethoxilated polyethylen-derivative, on the portion of the glass substrate including the ink composition.

4. The process of claim 3, wherein the adhesion promoter primer composition is prepared separately by adding 70% to 97% by weight of demineralized water and 0% to 19.4% by weight of ethyl alcohol and 0.15 to 3% by weight of a silane under stirring, and is applied as a thin layer on the glass substrate, before applying the ultraviolet curable organic ink composition. and dried on the glass substrate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MX 99/00038

| A. CLASSIFICATION OF SUBJECT MATTER | | |
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| IPC7 CIP ³ C09D 11/10. B41M 1/34 | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) | | |
| IPC7 CIP ³ C09D. B41M. C03C | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | |
| EPODOC. CAS. CIBEPAT, WPI | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | WO 9852700 A (REVLON CONSUMER PRODUCTS CORP.) 26 November 1998 (11.11.98) examples- and claims | 1-4 |
| A | Base de datos HCAPLUS en STN. AN 1996: 321209: JP 8048923 A (SAKURA COLOR P. CORP.) 20 February 1996 (20.02.96) abstract | 1-4 |
| A | EP 604815 A (CERDEC AKTIENGESELLSCHAFT KERAMISCHE FARBEN) 06 April 1994 (06.04.94) examples 1-4, - claims | 1-4 |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. | | |
| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> | | |
| Date of the actual completion of the international search | | Date of mailing of the international search report |
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| Name and mailing address of the ISA/ S. P. T. O | | Authorized officer |
| Facsimile No. | | Telephone No. |

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
 information on patent family members

 International Application No
PCT/ MX 99/00038

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| WO 9852700 A | 26.11.1998 | ZA 9804363 A NO 995719 A AU 7595598 A | 30.11.1998 24.01.2000 11.12.1998 |
| EP 0604815 A | 06.07.1994 | DE 9309796 D AT 184902 T US 5411768 A US 5346933 A CA 2112552 A BR 9305276 A JP 6228493 A | 28.10.1999 15.10.1999 02.05.1995 13.09.1994 01.07.1994 05.07.1994 16.08.1994 |
| JP 8048923 A | 20.02.1996 | NONE | |

Form PCT/ISA/210 (patent family annex) (July 1992)